Full length article

Effect of oxygen defects blocking barriers on gadolinium doped ceria (GDC) electro-chemo-mechanical properties

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ABSTRACT

Some oxygen defective metal oxides, such as cerium and bismuth oxides, have recently shown exceptional electrostrictive properties that are even superior to the best performing lead-based electrostrictors, e.g. lead-magnesium-niobates (PMN). Compared to piezoelectric ceramics, electromechanical mechanisms of such materials do not depend on crystalline symmetry but on the concentration of oxygen vacancy ($V_O^-$) in the lattice. In this work, we investigate for the first time the role of oxygen defects configuration on the electro-chemo-mechanical properties. This is achieved by tuning the oxygen defects blocking barrier density in polycrystalline gadolinium doped ceria with known oxygen vacancy concentration, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$, $\delta \approx 0.05$. Nanometric starting powders of ca. 12 nm are sintered in different conditions, including field assisted spark plasma sintering (SPS), fast firing and conventional method at high temperatures. These approaches allow controlling grain size and Gd-dopant diffusion, i.e. via thermally driven solute drag mechanism. By correlating the electro-chemo-mechanical properties, we show that oxygen vacancy distribution in the materials plays a key role in ceria electrostriction, overcoming the expected contributions from grain size and dopant concentration.

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1. Introduction

Cerium oxide ($\text{CeO}_2$) has been comprehensively investigated in the last few decades due to its multifold applications, more specifically in electro-ceramics and catalysts [1—4]. It has a centrosymmetric fluorite structure with a pronounced oxygen defectivity, i.e. oxygen vacancies ($V_O^-$). This feature makes ceria an excellent ionic conductor, especially suitable for solid-state electrolytes at high temperatures [5], where acceptor dopants are used to enhance oxygen defects concentration, $[V_O^-]$ in the lattice [6,7]. In cerium oxide, Ce$^{4+}$ cation can also be reduced to Ce$^{3+}$ under low oxygen partial pressure ($P_{O_2}$) at high temperatures, creating both quasi-free localized electrons, i.e. small polarons and oxygen vacancies [8], resulting in mixed ionic-electronic conductivity (MIEC) [5,9]. Besides these properties, ceria exhibits non-classical giant electrostriction at room temperatures [10—12], both in thin films and bulk materials. Remarkably, ceria thin film expands perpendicular to applied field direction, with large compressive stress ($\approx 500 \text{ MPa}$) [10]. The average electrostriction coefficient ($M_e$) is reported as $\approx 6.5 \cdot 10^{-18} \text{ (m/V)}^2$ for $[V_O^-] = 5\%$, i.e. 20 mol% Gd-doped ceria [10]. Such value is high for a material with low dielectric constant ($\varepsilon_{\text{GDC}}\approx 30$) [13], even higher compared to relaxor ferroelectric metal oxides, e.g. Ca-doped PMN ($\varepsilon_{\text{Ca-PMN}} \approx 4000$) [14]. Yavo et al. also verified this type of electromechanical properties in bulk gadolinium doped ceria and another oxygen defective fluorite oxide ($\text{Bi}_2\text{O}_3$), which exhibit similar results, thus representing to a new class of electroactive materials [12,15]. The atomistic model proposed by Lubomirsky et al. based on XANES/EXAFS measurements [16] comprehensively explains the underlying phenomena of this unusual behavior, further suggested that the presence of oxygen vacancy makes distorted Ce$^{3+}$--$O_2^-$ units: consisting of contracted Ce--O and expanded Ce--$V_O^-$ bond, compared to Ce--O bond in Ce--$8O$ unit [10,16]. As a result, asymmetric charge
distribution and anisotropic local dipolar elastic field are developed in the fluoroite lattice [17]. Under the applied electric field, distorted CeCe\textsuperscript{−}7O\textsubscript{6}−V\textsubscript{G} complexes conform to more fluoroite-like structure and subsequently, local atomic displacement produces giant electromechanical effect [16]. Despite intriguing, some questions about the role of oxygen vacancies and microstructure on electrostriction still remain unexplored [12]. Besides, Lubomirsky and co-workers suggested a power-law dependence of I−V relationship in grain boundary blocking behavior based on space charge mechanisms [18,19] and demonstrated that an increase of grain boundary resistance leads to a decrease in the portion of applied voltage drop in the bulk, decreasing electromechanical properties [20].

As ion conductor at high temperatures, bulk properties of ceria-based compounds are controlled by process parameters, i.e. morphology of initial powders, sintering kinetics/thermal history, densification, final microstructure, etc. For sintering and consolidating, mass diffusion mechanisms are especially dominated by solute drag phenomena, which, depends on both dopant size and valence. These can influence ionic configurations at the grain boundary, for instance, by trapping vacancies in disorder and/or in vacancies-ions complexes with low mobility [21,22]. This is described by the so-called "brick model" that is observed for highly defective ceria where fast ionic migration mechanisms are activated, thus reducing cations trapping effects at the grain boundaries [23–26]. Solute drag phenomena create specific grain boundary configurations and non-stoichiometry, which acts as blocking barriers to migrate charge species in the material, significantly affect intrinsic properties [21]. Moreover, Shibata et al. experimentally showed that the long-range electric interaction is the governing factor in controlling the local charge distribution at the crystal interface [27].

Based on previously published reports, designing the microstructure at nano-scale is also expected to create more significant differences between oxygen migration effects, revealing dissimilar physical and chemical properties than a grain of micron sizes. In addition, decreasing the grain size leads to increase grain boundary effect on the material, as well as increasing the density of the blocking barrier [28]. On the other hand, Esposito et al. proposed that grain boundary blocking factor is not necessarily a geometrical factor [3]: at a fixed oxygen vacancy concentration, different grain boundary blocking effects are encountered, depending on the entity of solute drag effect, controlled by sintering conditions [3]. The grain boundary blocking effect is explained both theoretically and experimentally by the distribution of defects by space charge layer model [29–35]. Other techniques also can disrupt the solute drag effect, even maintaining the polycrystalline in the nanoscale. This occurs by field assisted sintering techniques (FASTs), such as spark plasma sintering (SPS) [36]. FASTs use three important parameters (i) pulsed electric field, (ii) high heating rates and (iii) high pressure to preserve ultra-fine grains [37,38].

In the present work, we use nanometric 10 mol % gadolinium doped ceria (GDC10) to produce polycrystalline samples with different oxygen vacancy configuration. This is done by sintering the nano-powders by field assisted (SPS), fast firing and conventional method, which yields dense polycrystalline samples with tuned oxygen ions blocking barriers. A commercial high-density tape cast sample with minimized grain boundary is also used for comparison. The influence of oxygen vacancy configuration on electro-chemo-mechanical properties of GDC was investigated, comparing the electrochemical properties from low to intermediate temperatures (ca. 300−575 °C) with the electromechanical properties at room temperatures, expecting unchanged oxygen vacancy configuration in the materials.

2. Experimental procedure

2.1. Powder synthesis

Nano size gadolinium doped ceria (GDC10) powders were prepared by co-precipitation method using diamine in aqueous solution [3]. Cerium nitrate hexahydrate (Sigma-Aldrich, USA) and gadolinium nitrate hexahydrate (Sigma-Aldrich, USA) salts were mixed together in stoichiometric proportions to prepare 0.1 M solution in deionized water. Then MDEA (N-methyl-diethanolamine) was added dropwise. The resulting gel was dried at 120 °C followed by calcination at 500 °C for 2 h. After the calcination, hard agglomerated powders were ball-milled in ethanol with 2 mm zirconia balls for 10−12 h at 50 rpm, followed by drying at 120 °C for 10 h. Finally, the powders were softly crushed by mortar and pestle and sieved using a 150 μm mesh.

2.2. Pellet preparation

The SPS sample was consolidated by field assisted spark plasma sintering (SPS) (Dr. Sinter Lab 5155, Japan) under high vacuum (<6·10<sup>−6</sup> Torr) at 980 °C, uniaxial pressure of 70 MPa with 5 min dwelling. To minimize the chemical reduction that may occur by FAST treatments, the sample was re-oxidized by post-heating at 700 °C for 1 h. For the conventional sample, powders were uniaxially cold pressed at 200 MPa for 30 s, followed by sintering at 1450 °C in air for 10 h. To achieve high density in the pellets independently by the powders packing [39], the fast-fired sample was pre-densified by SPS at 900 °C and then thermally treated at 1450 °C for 0.1 h with 20 °C/min heating and cooling rate. Commercial tape (Kerafol Germany) was sintered at 1450 °C for 2.5 h.

2.3. Materials characterization

The density of the samples was measured in water using Archimedes method. The particle size and phase composition of the samples were analyzed by transmission electron microscope (TEM) (JEOL 2100, USA) and X-ray diffraction technique (XRD) (Bruker D8, Germany), respectively. The microstructure was investigated by a high-resolution scanning electron microscope (SEM) (Zeiss Merlin, Germany). The grain sizes were calculated by the linear intercept method using a minimum of 100 grains, multiplying with correction factor 1.57 [40]. The electrochemical impedance spectroscopy (EIS) was performed at 300−575 °C in air using Solartron 1260 (UK), in a frequency range of 0.01 Hz−1 MHz with a 100 mV alternate signal. The samples have bar-like geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry. Gold-silver mixture electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration geometry.
PZT (Shenzhen Yuije Electronics Co. Ltd. China). The sample was pressed between two metal electrodes using a spring. A pushrod is used to transfer displacement from the electrodes to a proximity sensor. The signal from the proximity sensor is captured using a lock-in amplifier. Longitudinal electrostrictive strain (parallel to the applied electric field) is calculated as a ratio between the displacement and the original thickness of the ceramic pellets.

3. Results and discussion

Use of nano-powder in ceramic processing allows fine control of the microstructural features in final bulk materials. The morphology and structure of the starting nano-powder used in this work are shown in Fig. 1. TEM analysis revealed that particles have a spherical shape and are loosely agglomerated. The nano-powders have a narrow range of size distribution with an average particle size ranging between 10 - 15 nm. Electron diffraction pattern shows fluorite symmetry of ceria. Crystallography was further confirmed by X-Ray diffraction technique.

Fig. 2 illustrates the XRD pattern of GDC powder and sintered samples. Within the detection threshold of the technique, the patterns reveal no secondary phases. The reflection peaks of the pattern perfectly fit with the theoretical pattern (ICSD code 251473). Average crystallite size by Scherrer and lattice parameter for the starting powders are estimated as ≈ 12 nm and 0.540 nm, respectively. Results are consistent with the TEM analysis in Fig. 1. For the sintered samples, XRD patterns in Fig. 2 also display identical results. Narrow peaks imply an increase of particle size during sintering, according to the Scherrer formula [41].

The microstructures of sintered GDC samples are presented in Fig. 3. The micrographs indicate that grains are highly dense with negligible intra-granular porosity. The outcome is consistent with the experimental density of the pellets, which is above 96%, for all samples. Grain size analysis shows that both the SPS and fast firing sample have a significantly smaller grain size (around 150 – 200 nm) than conventionally sintered materials. They exhibit typical polygonal grains with nearly homogeneous size distribution. Furthermore, they show no surface relaxation at the grain boundary. Plapcianu et al. found similar results in SPS sintering of GDC [37]. These authors stated that restricted grain growth in this type of non-conventional sintering is attributed to fast heating rates especially in the initial stage of sintering, where grain-coarsening mechanism dominates. However, GDC-10 h and GDC-2.5 h materials show a high degree of grain growth with an average grain size of 2.0 ± 0.3 μm and 1.5 ± 0.2 μm, respectively. Nearly all grains have equilibrium shape at the triple point (red lines in Fig. 3c, 3d) with fully relaxed and residual small grain boundary curvature (see black arrows in Fig. 3c, 3d).

Fig. 4a and Fig. 4b illustrates the geometry normalized Nyquist plots (ρ’ vs ρ”) at 300 °C. The geometrical normalization is carried out for the total volume of the samples, to have a direct comparison between the materials, and it does not take into account the actual volume fraction of the grain boundary in the sample. These Nyquist spectra were fitted by using parallel equivalent circuits of RQ element. R is denoted as resistor and Q is termed as constant phase element, as $C = \frac{(R^{-1} + Q)^{-1}}{n}$, where C is the capacitance and n is the fitting parameter. At this temperature, as evident from Fig. 4a, only one semicircle is observed in both the nanostructured GDC-SPS and GDC-0.1 h samples, which correspond to strongly overlapped bulk and grain boundary contribution, with capacitance representing the bulk value (see Table 1). Similar features were previously reported in other studies on nanocrystalline ceria materials, suggesting superimposed semicircle is predominated by grain boundary impedance [42,43]. Tuller et al. stated that such overlapping behavior is due to the similar order of magnitude between the space charge width and grain size [44]. Since deconvolution of bulk and grain boundary contribution from these samples is not possible and due to the typical frequency response, the single semicircle is attributed to the grain boundary. On the other hand, conventionally sintered microcrystalline GDC-10 h and GDC-2.5 h samples display two well-defined semi-circles (see Fig. 4b) that according to brick layer model, refer to the high and intermediate frequency associated bulk and grain boundary impedance, respectively [45]. The low frequency arc attributes to the electrode/material interface polarization mechanisms that are not relevant for this discussion [46]. Both GDC-10 h and GDC-2.5 h samples exhibit a comparable bulk resistance, however, distinct grain boundary resistance is measured. The effect of grain boundary
resistance is characterized by the grain boundary blocking factor ($a_{gb}$), which is defined as the ratio of grain boundary resistance to the total resistance ($a_{gb} = \frac{R_{gb}}{R_{total}}$) [47]. The grain boundary blocking factor ($a_{gb}$) is estimated as $\approx 0.65$ and $\approx 0.9$ for GDC-2.5 h and GDC-10 h at 300 °C, respectively. Comparing the microstructure, such behavior is unexpected as GDC-10 h has larger grain size, i.e., lower gb/grain geometrical ratio, than GDC-2.5 h sample.

Similar results were previously reported, where long-term thermal treatment, i.e., 36 h, possesses a detrimental effect on the blocking factors for low dopant concentration, e.g., for the conventional sintering for 10 h [3]. Furthermore, a significantly higher resistance in GDC-SPS compared to GDC-10 h indicates a field assisted trapping of oxygen vacancies in the lattice during SPS. High electric fields in SPS can result in a frozen non-equilibrium dopant.
distribution, which could decrease the possible vacancy mobility in the nanometric polycrystalline materials. Moreover, one report suggests that the chemical reducing condition occurring during the SPS can also create a large number of Ce\(^{3+}\) species that remain confined at the grain boundary, even after long time re-oxidation [36], resulting in an increment of grain boundary space charge potential. As mentioned before, nanostructures in SPS create a high density of grain boundaries, which act as a high blocking barrier to charge migration [48,49]. Although having similar nanostructure like GDC-SPS, fast firing sample, i.e. GDC-0.1 h presents an intermediary behavior between GDC-SPS and GDC-10 h. To sum up, all the samples possess similar density and exactly same dopant concentration, however, they develop quite different grain boundary resistance (blocking barrier), an effect that is ascribed to dissimilar oxygen vacancy configurations. In a broader sense, various sintering mechanisms lead to govern unlike oxygen vacancy configurations in the material, as well as dissimilar ordering of vacancies and defect hopping probabilities, which could be attributed to the nature of solute drag effect due to various thermal treatments.

In Fig. 4c, \(\rho\) vs frequency plots elucidate the distribution of charge transport by means of its relaxation frequency. Both GDC-10 h and GDC-2.5 h expose a bulk relaxation frequency around ~200 kHz, while, grain boundary relaxation frequency exhibits around 1.5 kHz and 20 kHz (data not shown here), respectively. Such a low grain boundary frequency response is attributed to high blocking barrier effect in the GDC-10 h compound. GDC-SPS and GDC-0.1 h show an overlapped relaxation frequency at 1.2 kHz and 5 kHz, respectively. This overlay behavior is ascribed to different charge transport mechanism, as resulting from unrelaxed microstructure and non-equilibrium fast thermal treatment. Above all, comparative analysis of high frequency response (see inset Fig. 4c) suggests that possible bulk relaxation behavior of GDC-0.1 h is equivalent to GDC-10 h sample, while GDC-SPS show very limited response.

Table 1 summarizes the capacitance, relaxation frequency values of the samples at 300 °C, along with average grain size. These values are calculated from the constant phase element with the 1/RC relationship from the fitted plots.

The temperature dependence of the total electrical conductivities (\(\sigma = 1/\rho\)), i.e. bulk plus grain boundary is illustrated with an Arrhenius plot in Fig. 5a. As anticipated and observed, conventionally sintered microcrystalline samples display superior electrical conductivity than non-conventional nanocrystalline materials. Additionally, it is worth mentioning that at high doping content such as 10 mol% Gd, electronic conductivity is negligible at atmospheric pressure [50], therefore it can be assumed that total electrical conductivity (bulk and grain boundary) in air is solely controlled by the migration/mobility of \(V_{O}^{\cdot}\). GDC-2.5 h displays highest electrical conductivity among all of them, whereas, GDC-SPS displays the minimum, which is directly interlinked with activation energy values. The high activation energy in GDC-SPS is also consistent with the existence of a large density of blocking barrier illustrated in Fig. 4, an effect conceivably caused by vacancy trapping or/vacancy clustering mechanisms. The minimum activation energy observed in GDC-2.5 h could be of different grain boundary composition (uniform dopant distribution) due to short thermal treatment. GDC-0.1 h shows similar conductivity of previous work (see Fig. 5a), however, as expected, GDC-10 h sample displays much higher conductivity than GDC-36 h [3]. At the same time, Fig. 5b distinguishes between bulk and grain boundary conductivity for GDC-10 h and GDC-2.5 h samples. In this case, the resistivity of the two contributions is normalized by the actual volume of bulk and grain boundaries, as reported in Ref. [50]. According to expectations, microcrystalline samples show a similar trend in bulk conductivity. A significant difference is determined in grain boundary conductivity value, which is linked to the grain boundary blocking factor. Low grain boundary conductivity in GDC-10 h also confirms that oxygen vacancy at the grain boundary is less mobile than GDC-2.5 h sample. The most substantial result is that measured ionic conductivity of GDC-0.1 h lies in between grain boundary conductivity of GDC-10 h and GDC-2.5 h samples, at these temperatures range. This outcome further presupposes that grain boundary blocking factor (\(\gamma_{gb}\)) in GDC-0.1 h sample might be in between 0.65 and 0.9. Additionally, it supports the hypothesis that the conduction mechanism in nanocrystalline ceria is ruled by grain boundary blocking factors.

The electrostrictive strain as a function of applied electric field square is presented in Fig. 6. All the compounds exhibit negative longitudinal strain that agrees with previous reports of GDC thin films and bulk materials [10,12]. They respond at the second harmonic of the applied electric field with different frequency within the applied range, further confirming its electrostriction behavior. Besides, the graph explains the following trends i.e. at low frequency, the strain saturates with increasing electric field amplitude, whereas with increasing frequency magnitude of strain value declines dramatically. The strain saturation behavior empirically fits the following equation:

\[
\mu(E^2) = M_{13} \cdot E_{sat} \cdot \left[1 - \exp\left(-\frac{E^2}{E_{sat}^2}\right)\right]
\]  

Where \(M_{13}\) is the electrostriction 3-3 strain coefficient and \(E_{sat}\) is the saturation electric field. Beyond the saturation point, the linear relationship between electrostriction strain vs \(E^2\) is no longer valid. At certain electric field and frequency, GDC-10 h shows maximum electrostrictive strain among all the samples, which has a high bulk and low grain boundary relaxation frequency (see Fig. 4c). Surprisingly, GDC-2.5 h, with low blocking barriers, exhibits \(M_{13}\) value much smaller than GDC-10 h. Furthermore, it does not show any strain saturation behavior, and strain linearly increases with \(E^2\). The reason for this effect could be of high grain boundary conductivity, which leads to a marginal voltage drop at bulk grain. On the other hand, being nanostructured and having higher blocking effect compared to GDC-2.5 h sample, GDC-0.1 h generates much higher electrostriction than counterpart does. The most surprising result is observed with GDC-SPS sample. The electromechanical response of this sample is significantly lower compared to others, for instance, electrostrictive strain coefficient (\(M_{13}\)) value being one order of magnitude lower than GDC-10 h. The small value of the former is not due to its unrelaxed grain size but connected to trapped ionic/electronic defects–cation association and its interaction with the electric field. These defect–complexes are neutral and do not respond at low electric fields, suggesting super blocking behavior at the grain boundary.

This significantly highlights the flexibility of the blocking barrier in tuning the electrostrictive strain. For high electrostriction, the barriers should block oxygen vacancy migration without meaningfully decreasing the potential drop and vacancy should resonate.

### Table 1

<table>
<thead>
<tr>
<th>Sample Item</th>
<th>(C_{\text{total}}) (F)</th>
<th>(f_{\text{total}}) (Hz)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDC-SPS</td>
<td>2.0 × 10(^{-11})</td>
<td>1.2 × 10(^{4})</td>
<td>200 ± 25</td>
</tr>
<tr>
<td>GDC-0.1 h</td>
<td>3.5 × 10(^{-11})</td>
<td>5.0 × 10(^{3})</td>
<td>170 ± 20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Item</th>
<th>(C_{\text{bulk}}) (F)</th>
<th>(C_{\text{G.B.}}) (F)</th>
<th>(f_{\text{bulk}}) (Hz)</th>
<th>(f_{\text{G.B.}}) (Hz)</th>
<th>Grain Size ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDC-10 h</td>
<td>1.2 × 10(^{-11})</td>
<td>3.0 × 10(^{-10})</td>
<td>2.0 × 10(^{3})</td>
<td>1.5 × 10(^{3})</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>GDC-2.5 h</td>
<td>2.9 × 10(^{-11})</td>
<td>4.0 × 10(^{-10})</td>
<td>2.0 × 10(^{3})</td>
<td>2.0 × 10(^{3})</td>
<td>1.5 ± 0.2</td>
</tr>
</tbody>
</table>
within the lattice, as per the model described by Lubomirsky et al. [16].

Fig. 7 demonstrates the declining trend of electrostrictive strain coefficient ($M_{33}$) with increasing frequency. This type of electrostriction relaxation with frequency can be fitted by (non-ideal-Debye) following function:

$$M_{33}(f) = \frac{M_{33}^0}{\sqrt{1 + (\tau f)^2}} + M_{33}^\infty$$

Here, $M_{33}^0$ and $M_{33}^\infty$ are frequency independent electrostriction coefficient, $\tau$ is the relaxation time and $\alpha$ is detonated as a non-ideality factor. Both the saturation and relaxation phenomena are observed in the recent publication of Yavo et al. [12], specifying that both mechanisms are intrinsic properties of electromechanical behavior of gadolinium doped ceria. Moreover, $M_{33}$ values are approximately in order of \(10^{-18}\) (m/V)\(^2\) at 10 Hz for all the samples, which are still one order of magnitude higher than the classical electrostriction model.

Table 2 describes the comparative analysis of grain boundary resistivity and electrostriction coefficient among the samples. Finally, by correlating experimental findings, it can be concluded that electrostriction in GDC materials increases with grain boundary blocking factor up to a certain level (below super blocking...
region) and then decreases dramatically. The effect of blocking in electrostriction is also schematically presented in Table 2. The blocking diagram and the data strongly suggest that electrostriction is not dependent on the geometrical ratio between bulk and grain boundary. Microstructure does not necessarily influence the electromechanical properties. Additionally, it also confirms that the nominal oxygen vacancy concentration is not a true parameter that controls electrostriction. In conclusion, it is the blocking barrier at the grain boundaries, which regulates the electrostrictive properties. The blocking barrier is tuned by the configuration of oxygen vacancy within the grain boundary. Despite more uniform oxygen vacancy distribution, both GDC-SPS and GDC-0.1 h materials show considerably limited electromechanical activity compared to GDC-10 h with a low density of large blocking barriers. These results finally conclude the dominant distribution of oxygen defect configuration to the electromechanical properties.

4. Conclusion

In this work, highly dense GDC ceramic pellets were fabricated by both non-conventional and conventional sintering methods. Non-conventional sintering was performed by SPS and fast firing to achieve similar nanometric microstructures with tuned oxygen vacancy configurations, with the same nominal oxygen vacancy concentration. The resulting polycrystalline materials exhibit un-relaxed microstructure with nano-grains, while the samples sintered in conventional method exhibits equilibrium grain of micron size. Surprisingly, electro-chemo-mechanical properties of the samples did not follow a mere geometrical grain size dependency. They show a strict dependency on ionic migration blocking barriers built in the materials by the different sintering processes. Furthermore, all the compounds show non-classical giant electrostriction with a strong dependency on the frequency and electric field amplitude. Above all, it was observed that sample with high bulk and low grain boundary relaxation frequency exhibits large electrostrictive coefficient, which is further related to the distribution of oxygen vacancies. In summary, the oxygen defects configuration rather than their nominal concentration in the bulk controls the electromechanical behavior in Gd-doped ceria.

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